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A study of the relaxation of discommensurations in K_2ZnCl_4: II. Dielectric measurements at low frequency

Xiaoqing Pan and H-G Unruh

Fachbereich 10—Physik, Universität des Saarlandes, D-6600 Saarbrücken, Federal Republic of Germany

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Abstract. The quasi-static dielectric constant and ferroelectric hysteresis in K_2ZnCl_4 were studied. In the virgin crystals, the dielectric constant exhibits a remarkable time-dependent variation during repeated temperature cycling and annealing. These results may be interpreted by assuming different nucleation probabilities of discommensurations (DC) in the virgin crystals and in those which had been heated to the incommensurate phase, and by considering the defect pinning of DC. It has also been found that the coercive field of the ferroelectric hysteresis exhibits a monotonic increase with time in the C phase. This is attributed to a gradual decrease of the DC density by vanishing of DC. With a model for the influence of crystal defects on the distribution of DC, the experimentally measured data have been well fitted.

1. Introduction

In the last decade structurally incommensurate (I) systems have been the subject of intensive theoretical and experimental investigations. Crystals of A_2BX_4 type constitute a large family of these systems (Blinc and Levanyuk 1986, Cummins 1990). They all present a similar sequence of structural transitions. A prototype N phase undergoes a second-order transition at T_I into an incommensurately modulated phase, and then reaches a low-temperature ferroelectric commensurate (C) phase passing through the I–C transition at T_C. One of the widely studied characteristics is the existence of discommensurations (DC). In the lower temperature range of the I phase the structure of the system consists of numerous nearly commensurate regions separated by DC, and the transformation during the C–I transition proceeds through nucleation or annihilation of DC. Such processes may be directly observed by transmission electron microscopy (TEM).

Among the A_2BX_4 family, K_2ZnCl_4 exhibits some specific properties, such as a rather pronounced hysteresis and slow time evolution of the dielectric constant (Unruh 1984, Zhang *et al* 1985, Ema *et al* 1985). The interpretation of these phenomena requires a study of the properties of the DC and their significance for the C–I transition. Direct observations of DC by TEM should give insight into the understanding of these phenomena. The first part of our studies on the DC and their relaxation was confined to this aspect (Pan and Unruh 1990). In this work the characteristic patterns mainly show regularly arranged DC. Vortices are formed by three pairs or six isolated DC. Direct observations with TEM also revealed rearrangements of DC after some DC had vanished or after prolonged irradiation by the electron beam. However,

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observations of the time relaxation of DC density and of the transformation processes during the C–I transition at $T_C \simeq 403$ K are limited by serious irradiation damage of samples. Therefore, supplementary studies to TEM are required to understand fully the properties of DC and their significance in the C–I transition.

The I–C transitions are ferroelectric in the case of K_2ZnCl_4. The DC in this case are considered to be plane defects separating two oppositely polarized regions in the I phase, and ferroelectric domain walls in the C phase. Therefore, dielectric measurements may reveal the average behaviour of the DC. Assuming that the static dielectric constant is proportional to the density of DC, one may study the processes of nucleation (or annihilation) and the evolution of DC during the C–I transition (Sakata *et al* 1990), and even obtain information about the interaction of DC (Levstik *et al* 1987). In addition to observations by TEM, the mobility of DC can also be probed in an approximate way by investigating the ferroelectric hysteresis. Furthermore, the study of the frequency-dependent complex dielectric constant $\epsilon^*(\omega)$ may extend the information on the induced polarization in the I structures and its dynamics. Owing to the characteristic form of the modulation near T_C, i.e. the DC-like modulation, the study of the dielectric dispersion can also provide information about the processes of the I–C transitions by observing the temperature and time evolution of the dispersion. Therefore, the specific properties of K_2ZnCl_4 mentioned above may be understood by supplementary dielectric studies to the TEM observations.

In the present paper we present the experimental studies of measurements of the quasi-static dielectric constant and of the ferroelectric hysteresis. The results will be discussed on the basis of Landau theory and of a fundamental model of defect pinning on DC. The investigations of dielectric dispersion will be given in a separate paper (Pan and Unruh 1992).

2. Experimental methods

K_2ZnCl_4 crystals were grown from aqueous solutions of a stoichiometric mixture of KCl and $ZnCl_2$ at about 313 K. The *b*-plate samples of about 20 mm^2 in area and 0.5 mm in thickness were cut using a wet thread. For dielectric measurements these platelets were provided with evaporated gold electrodes. The dielectric constant was measured with a bridge, an HP 4275A Multi-Frequency LCR Meter. The data were recorded with an HP computer. The measurement of the dielectric hysteresis was taken by a Sawyer–Tower circuit with compensation of specimen conductivity. The same specimens as for the dielectric measurements are used for the hysteresis measurements.

3. Experimental results

3.1. Measurements of the quasi-static dielectric constant

The complex dielectric constant at 10 kHz was measured within several thermal cycles for virgin crystals grown at 313 K in the ferroelectric C phase. Upon increasing the temperature at a rate of 2 K min^{-1} the dielectric constant was observed to be about 12 below T_C and showed a very small increase at about 410 K (see curve 1 in figure 1(*a*)). During subsequent thermal cycles curves 2 to 8 (figures 1(*a*) and (*b*)) were obtained. As shown in table 1, the thermal treatments included several annealing

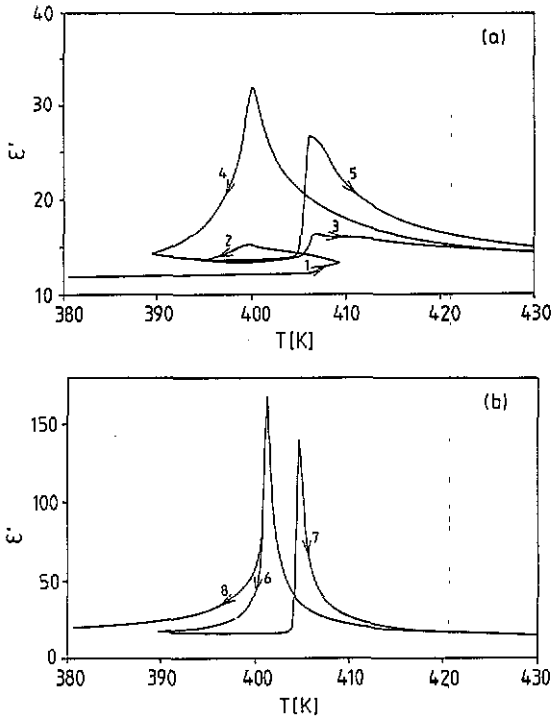

Figure 1. Temperature dependence of the dielectric constant of a crystal of K_2ZnCl_4, measured parallel to the ferroelectric axis at 10 kHz. Details of the thermal treatments are listed in table 1.

Table 1. The thermal treatments of the sample of K_2ZnCl_4 while measuring the dielectric constant corresponding to figure 1.

Initial temperature (K)	Final temperature (K)	Rate (K min^{-1})	Duration [a] (h)	Curve number
20	390	2	0	
390	410	0.5	0	1
410	390	0.5	0	2
390	433	0.5	4	3
433	390	0.5	0	4
390	450	0.5	18	5
450	390	0.1	0	6
390	450	0.1	18	7
450	401	0.5	0	8
401	390	3.5	0	8

[a] The time for which the sample was stabilized at the final temperature of the thermal run.

processes. Figure 1(*b*) shows that the sample finally exhibited very sharp peaks of about 170 (curves 6 and 8) on cooling and 140 (curve 7) on heating, respectively.

It was noted that during the first heating the dielectric constant of a 'virgin' crystal depends neither on temperature nor on time below about 400 K. However, this is no longer true at a temperature above 400 K and for the samples that had once been heated to the I phase. According to the observations by Sakata *et al* (1990),

'virgin' crystals of K_2ZnCl_4 are practically free of DC. Therefore, one may conclude that the time dependence of ϵ' is associated with the evolution and rearrangement of DC patterns in the sample, which is a relatively slow process with a time constant of several hours. Studies of these phenomena were reported by many authors (Unruh 1984, Mashiyama and Kasatani 1985, 1987, Zhang *et al* 1985, Sakata *et al* 1990).

According to the Landau theory of I systems (Levstik *et al* 1982, Mashiyama and Unruh 1983), the movements of DC in response to the measuring field result in the so-called anomalous part of the dielectric constant, which is proportional to the density of DC. On this assumption the density of DC can indirectly be determined by measurements of the dielectric constant, and the dielectric 'tails' below T_C can thus be attributed to a certain density of DC in the C phase. However, the existence of a pronounced thermal hysteresis and the different shapes of measured curves in figure 1 have to be analysed by taking the processes of nucleation, annihilation and rearrangement of DC into account. Furthermore, the I and C phases may coexist in the crystal, and pinning effects of DC by crystal defects may play a significant role in the experiments.

3.2. Measurements of the ferroelectric hysteresis

In the case of K_2ZnCl_4 the observation of the dielectric hysteresis near T_C is difficult, as the conductivity of the sample is high and the hysteresis curve is therefore distorted. Thus, all the ferroelectric hystereses presented in the following were recorded at ambient temperature (295 K). Furthermore, the virgin samples must be thermally cycled through the C–I transition because it is practically impossible to repolarize the virgin crystals (Gesi 1978, Pan and Unruh 1990). In order to get a suitable density of DC the virgin samples were annealed at 450 K and then quenched to ambient temperature. All the samples used had experienced the same process of thermal treatment as shown in table 2. The hysteresis loops were recorded directly after the sample reached 295 K.

Table 2. Thermal cycles experienced by the samples used for measurements of the dielectric hysteresis.

Initial temperature (K)	Final temperature (K)	Rate (K min^{-1})	Annealing time (h)
20	390	2	0
390	420	0.5	0
420	390	0.5	0
390	450	0.5	20
450	401.5	0.5	0
401.5	295	~3	0

Just after ambient temperature was reached, the hysteresis loop was smooth and slanted but gradually became steeper, and the saturation polarization approached a 'maximum' after about an hour. The four stages of these processes are reproduced in figure 2. The remanent polarization P_r as read from the loops increased within a few hours from zero to about 0.2 $\mu C\ cm^{-2}$ and then remained constant (figure 3). However, most surprising and interesting is the monotonic increase of the coercive (or threshold) field E_c with time. This effect is very pronounced during the first few hours just after cooling. It was found that E_c still increased after three weeks

while the loops remained upright, as shown in figure 2. After storage at ambient temperature for a few months, because of the further increase of E_c the samples were no longer repolarizable and electrically broke down at a field strength of about 10 kV cm^{-1}.

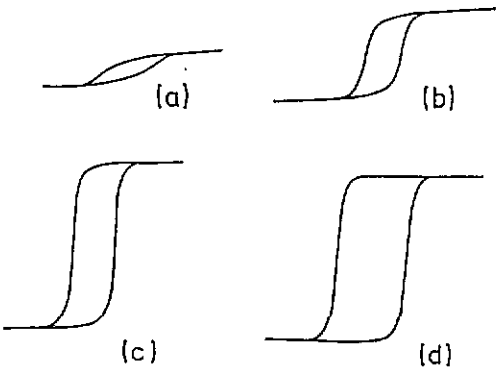

Figure 2. A sequence of hysteresis loops of a sample of K_2ZnCl_4 recorded at different time intervals after cooling the sample to ambient temperature: (*a*) 3 min; (*b*) 10 min; (*c*) 5 h; (*d*) 2 weeks (E scale compressed by a factor of 2).

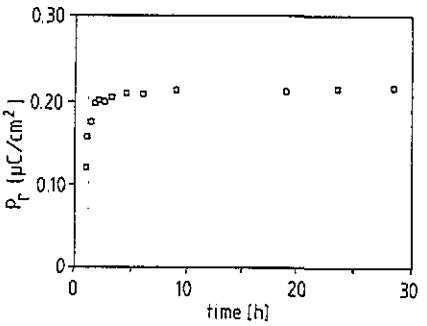

Figure 3. Time dependence of the remanent polarization of K_2ZnCl_4, measured from the hysteresis loops after cooling to ambient temperature.

In order to determine whether the increase of E_c is induced by the applied AC field (about 8 kV cm^{-1}), two kinds of experiments were carried out. In one case the alternating field was applied to the sample only when recording the hysteresis. In the other case it was applied throughout the whole experiment. Figure 4 shows the results obtained from two samples, which were cut from the same crystal. The data plotted by squares were obtained under the former condition, while the others (diamonds) were obtained under the latter one. The time $t = 0$ corresponds to the moment when the sample was cooled through T_C. As seen from figure 4, after about 15 h the increase of E_c in the sample without the field was larger than in the other case.

It is worthwhile to point out that the results mentioned above are not quantitatively reproducible in repeated experiments even with the same sample. This may be expected from the fact that it is impossible to get the same distribution and number of DC in different experiments. Moreover, the long annealing times at high temperature increased the conductivity and thereby reduced the quality of the crystal. However, the qualitative characteristics of the results are reproducible.

4. Discussion

4.1. Static dielectric properties of K_2ZnCl_4

In the I structures of the A_2BX_4 family the modulation of the lattice is connected with the appearance of a spatially varying polarization. In the C phases these materials behave as ferroelectrics with a finite spontaneous polarization. On the basis of the Landau theory the polarization of these systems arises from the high-order

(non-linear) coupling to the primary order parameter (Levanyuk and Sannikov 1974, Ishibashi 1980). Within the phase modulation approximation (PMA), in the case of $E = 0$ the minimization of the free energy leads to the time-independent sine–Gordon equation, which has an equally spaced DC solution on approaching T_C.

However, in the presence of an external field $E \neq 0$, the configuration of DC is distorted so that the width of domains polarized parallel to E is enhanced at the expense of the oppositely polarized ones (Levstik *et al* 1982). These authors also found that the dielectric susceptibility χ diverges at T_C on cooling from above according to the Curie–Weiss law $\chi \sim (T - T_C)^{-1}$. This means that near T_C the polarization modulation and thus the distance between adjacent DC becomes much more sensitive to the external field. This effect is attributed to the weakening of the DC interaction, which is exponentially dependent on the inter-DC distance within the PMA. According to the result of Blinc *et al* (1984), the dielectric constant in the vicinity of T_C can be written as

$$\chi - \chi_0 = [Cn_s/4\pi(T_I - T_C)]\exp(\pi/n_s) \qquad T > T_C \tag{1}$$

where n_s is the DC density, χ_0 the dielectric susceptibility in the C phase, and C a constant.

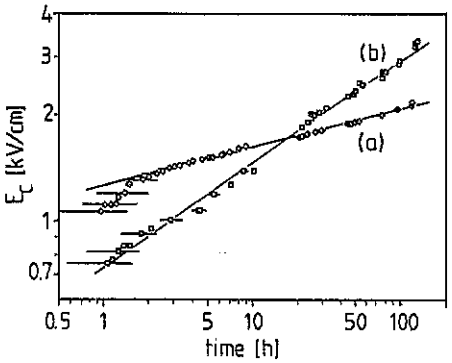

Figure 4. The time dependence of the coercive field E_c of K_2ZnCl_4, at ambient temperature. The data plotted as squares and as diamonds were obtained under different conditions (see text). The curves result from fitting equation (6) to the data. The parameters are: (*a*) $E_0 = 0.40$ kV cm^{-1}, $\gamma = 0.5$, $c = 15\,136$ (permanent AC field); (*b*) $E_0 = 0$, $\gamma = 7.85$, $c = 912$ (non-permanent AC field).

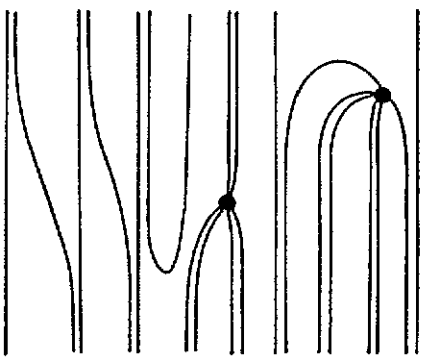

Figure 5. Schematic plot of possible configurations of DC in the C phase of K_2ZnCl_4 several months after cooling to ambient temperature.

The dielectric susceptibility in the C phase, χ_0, is expected to be independent of temperature. Therefore χ should jump from the maximum of the I phase to χ_0 at T_C on a cooling run. However, this is never the case in experimental observations, which show mostly a slow decrease of χ with decreasing temperature below T_C. From this point of view, by taking the pinning due to crystal defects into account and assuming a Gaussian distribution of the pinning fields E_i of the defects, Prelovsek and Blinc (1984) obtained the following expression for the 'anomalous part' of the dielectric susceptibility:

$$\Delta\chi = \chi - \chi_0 = (P/\pi\sigma_E)n_s \qquad T < T_C \tag{2}$$

where P is the spontaneous polarization just below T_C and σ_E the width of the Gaussian distribution. Therefore, the value of the dielectric tail is proportional to the DC density.

According to these theoretical considerations and in view of the processes of nucleation (or annihilation) and rearrangement of DC, the experimental results presented above can be understood as follows. The virgin crystal of K_2ZnCl_4 is DC-free. The nucleation of DC during the C–I transition requires a relatively high activation energy in the virgin crystal and may be considered homogeneous in the whole crystal, neglecting the crystal defects. As a result, it takes a relatively long time for the sample to transform from the C phase to the I phase at the transition temperature. In the second heating run there already exist some DC in the sample, which may work as cores of the nucleation of DC stripples (Unruh 1984). The nucleation of DC at such cores requires relatively small activation energy. Thus, the density of DC is higher than that obtained during the first heating run, and the dielectric constant therefore exhibits a slightly higher peak (see figure 1). After several thermal cycles the sample possesses many DC and therefore shows comparably sharp peaks of the dielectric constant in subsequent heating and cooling runs.

During annealing at a temperature well above T_C (at 450 K in our experiments), the sample has enough time for the rearrangement of DC and finally possesses a homogeneous DC lattice. On the subsequent cooling run, a high and sharp peak of χ is therefore obtained, as shown by curve 6 of figure 1(*b*). Furthermore, owing to the annealing of the sample many DC, which may be pinned by defects, will remain in the crystal after a fast cooling to the C phase. This results in a residual dielectric constant, or say dielectric tail, in the C phase, as expected by equation (2). This part of the dielectric constant is strongly dependent on the time because of a further annihilation of frozen-in DC. Nevertheless, unpinned DC can also remain in the C phase during a fast cooling, because the decrease of the DC density (mediated by the nucleation of vortices and their motions through the system) may proceed more slowly than the change of temperature. These DC will gradually vanish from the sample by thermal fluctuations. Afterwards, only the strongly pinned DC survive and the DC patterns in the crystal become complicated, as schematically plotted in figure 5. Such configurations of DC have been directly observed by TEM (Pan and Unruh 1990, Sakata *et al* 1990).

Gesi (1978) was the first to note the phenomena mentioned above, and he ascribed the broadness of the dielectric constant peak in a virgin crystal to the presence of a certain kind of lattice imperfection, which can be removed by annealing at temperatures above T_C. Zhang *et al* (1985) then noted that the increase of the dielectric anomaly near T_C after repeated temperature cycling and annealing coincides with a large reduction in the infrared absorption due to water. This result was inferred to be indicative of a major defect role of residual water in solution-grown crystals. The main difficulty of this interpretation is that the effect of annealing at a temperature above T_C is qualitatively different from that below T_C. In the latter case the peak of ϵ near T_C on a subsequent heating run is almost unaffected, in contrast with the former case. Moreover, for melt-grown crystals that have been stored at ambient temperature for several months, the peak of the dielectric anomaly also shows an increase after repeated temperature cycling and annealing, although in this case the amount of water in the crystal may be negligible.

Unruh (1984) also studied the time dependence of thermal hysteresis occurring on the dielectric constant with a step-like change of temperature and the relaxational

behaviour of ϵ of virgin crystals. He found that the thermal hysteresis is significantly reduced when the change of temperature is very slow and he explained the slow relaxational behaviour occurring in K_2ZnCl_4 as a result of the existence of defects, mainly pinned DC. Our explanation mentioned above is on the basis of this idea.

4.2. Time evolution of the discommensurations in the commensurate phase

The polarization reversal of ferroelectrics is usually considered to be driven by the nucleation of domain walls at the surface of the sample and the forward and sideward motions of these domain walls through the crystal. When the domains have expanded sideways sufficiently, they begin to coalesce with each other until all of the unswitched regions are completely 'overrun' by them. The coercive field E_c of the polarization reversal is a measure of the sideward mobility of domain walls.

However, there is no indication of nucleation and annihilation of DC during the polarization reversal in the C phase of K_2ZnCl_4. It has been found that virgin crystals could not be repolarized by fields of 15 kV cm^{-1} and a frequency of 0.1 Hz, while the values of E_c of freshly quenched crystals, which had been annealed at 450 K for several hours, were about 0.5 kV cm^{-1}. This is in accordance with the occurrence of extremely high values of E_c (> 20 kV cm^{-1}) observed in virgin crystals (Gesi 1978). Furthermore, the crystals of K_2ZnCl_4 used in our studies were grown in the C phase at about 313 K, and it has been found that virgin crystals possess almost no domain walls (Sakata *et al* 1990). From these points of view, nucleation of domain walls (i.e. DC) cannot be of importance during the process of polarization reversal. Therefore, the repolarization of K_2ZnCl_4 should be a consequence of the sideward motions of frozen-in DC through the crystal under an external electric field. Accordingly, E_c represents the mobility of DC and not a kind of nucleation threshold field. Thus, the increase of E_c with time presented in section 3.2 indicates the decrease of the mobility of DC.

The DC in the C phase are usually considered to be pinned by crystal defects. Therefore the mobility of DC is expected to depend strongly on the concentration of the defects. Directly after quenching to ambient temperature, the sample possesses a large density of DC, and the average pinning potential is weak. Thus, a small value of E_c is observed. When some DC vanish by the formation of stripples and their growth through the system, as directly observed by TEM (Pan and Unruh 1990), the average potential of the DC may increase owing to the diffusion of defects and the interaction between defects and DC. As a consequence, E_c exhibits an increase with time, as experimentally observed (figures 2 and 4).

On the other hand, an external field extends the domains polarized parallel to it while the oppositely polarized ones are reduced. At the end of the processes of repolarization the domains of the latter type do not vanish from the crystal but are compressed to narrow slices, the thickness of which is dependent on the applied field. As a consequence, the saturation polarization depends on the number of DC and the strength of the applied field. When the field is removed from the crystal, the slices expand to some extent owing to the interaction of DC. Therefore, the remanent polarization P_r mainly depends on the density of DC. Just after quenching to ambient temperature, there exists a large number of DC in the system, and thus only a small value of P_r is observed (see figures 2 and 3). Afterwards, P_r increases with time owing to the rapid decrease of the DC density, which is very pronounced during the first half an hour because of the probability of the nucleation of anti-stripples depending on the DC density. In accordance with this, P_r increases and then exhibits

no appreciable time dependence. This is in agreement with the experimental results shown in figure 3. In the following we present a qualitative interpretation of the time dependence of E_c on the basis of a simple model for the pinning states of DC.

Under an external electric field of low frequency, the DC are mostly in the paired or isolated state. However, TEM observations (Pan and Unruh 1990) indicated that DC only vanish six at a time. Therefore, the density of DC in the sample with an applied repolarizing AC field decreases more slowly than that without the field. Furthermore, the average pinning force of DC in the former case may be expected to be smaller than that in the latter case owing to the alternating field. As a result, the increase of E_c in the former case is slow with respect to that in the latter case, as experimentally observed (figure 4).

During annealing at T_A (450 K in the present case), it was assumed that a homogeneous DC lattice wsas formed in the sample. At the same time the crystal defects were concentrated in the vicinity of DC owing to their interaction with DC. The strength E of the pinning field per unit length of DC is randomly distributed through the sample, and may be assumed to have a Gaussian distribution, $g(E)$:

$$g(E) = (2\pi)^{-1/2}\sigma^{-1}\exp[-(E - E_0)^2/2\sigma^2] \tag{3}$$

where E_0 is the effective pinning field at which $g(E)$ exhibits its maximum, and σ the width of $g(E)$. Then, the number of DC with pinning field E is given by $n(E) = n_0 g(E)$, where n_0 is the DC number per unit area at T_A. Obviously E_0 depends on the concentration of the mobile defects at T_A. After quenching the sample to ambient temperature, the DC lattice becomes unstable and the density of DC decreases with time. On the other hand, the dielectric constant ϵ of K_2ZnCl_4 in the C phase (Mashiyama and Kasatani 1987) decays approximately according to an exponential law. Considering equation (2), the decay of the density of the DC that are pinned by an effective field E can be written as

$$n(E,t) = n(E)\exp(-t/\tau) \tag{4}$$

where $n(E)$ is the density of DC with a pinning field E at $t = 0$, and $\tau(E)$ the corresponding decay constant. The time at which the system passed through the I–C transition temperature (T_C) during the quenching is taken as $t = 0$. Furthermore, the probability of the decay of the density of DC decreases with increase of E. For simplicity, we assume $\tau = \tau_0 E^\gamma$, where τ_0 is a temperature-dependent constant, and γ a constant depending on the sample. From equations (3) and (4) we obtain

$$n(E,t) = (2\pi)^{-1/2} n_0 \sigma^{-1} \exp(-t/\tau_0 E^\gamma)\exp[-(E - E_0)^2/2\sigma^2]. \tag{5}$$

The meaning of equation (5) is as follows. In the beginning there is a certain distribution $n(E)$ of the density of DC with a maximum at $E = E_0$. This means that most DC are pinned by defects with a field E_0 after annealing at T_A. After quenching to lower temperature (e.g. to ambient temperature), the system gradually approaches the equilibrium state owing to the vanishing of many DC. This leads to many mobile defects, which are 'free' from DC. Simultaneously, the distribution of the point defects will be changed by further accumulation of these 'free' defects at remaining DC. As a result, most of the DC are pinned by a higher field $E' > E_0$, which makes equation (5) maximal. In other words, the effective pinning field of DC in the sample increases with increasing time.

In view of the definition of the coercive field E_c it is plausible to assume that E_c corresponds to E'. This means that most of the DC are forced to move when the applied field equals E'. By minimizing equation (5) we obtain

$$(E_c - E_0)E_c^{1+\gamma} - ct = 0 \tag{6}$$

where $c = \sigma/2\tau_0$. From equation (6) it follows that E_c increases with time. By choosing suitable values of the parameters E_0, γ and c, the experimental data can be fitted (figure 4). The values of the fitting parameters are given in the caption to figure 4.

5. Conclusions

In conclusion we have made an experimental study of the static characteristics and the dynamics of DC in K_2ZnCl_4 by means of measurements of the quasi-static dielectric constant at 10 kHz and ferroelectric hysteresis loops. We have also found that the pinning effects of DC by crystal defects play an important role in both the I and C phases. They enhance the thermal hysteresis and stabilize the DC in the C phase, resulting in the slow relaxation processes of the dielectric constant and an increase of E_c with time.

Furthermore, the slow relaxation processes of the C–I transition of K_2ZnCl_4 have also been revealed by an investigation of the frequency-dependent complex dielectric constant, which probes the dynamics of DC during the C–I transition. The analysis of the experimental data again shows that the nucleation and annihilation of DC and the pinning effects play an important role in the C–I transition in K_2ZnCl_4. The details of this study will be presented in a separate paper.

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